Communication

Response of the Devolatilization Process to the Lignin Concentration in Alfalfa Stems[†]

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Genetic modification or agronomic management of lignocellulosic biomass is considered a viable way of breeding the ideal bioenergy feedstock for renewable fuels. In fact, for biochemical conversion processes for producing lignocellulosic ethanol, lignin is considered a recalcitrant.[1,2] Hence, the so-called lignin engineering, i.e., research in lignin biosynthesis pathways,[3] has received increased attention. For thermochemical conversion, however, much has been made of lignin as being a high-quality combustion fuel. In a recent study, Boateng et al.[4] attempted to test this hypothesis by examining the response of thermochemical and biological conversion processes to the biological range of the lignin concentration in alfalfa stems (13 and 20 wt %) using *in vitro* gas production and high-temperature pyrolysis for the respective processes. The study found that the biological range of lignin concentration, although narrow, had a dramatic negative effect on *in vitro* ruminal fermentation, a surrogate of biochemical conversion potential. However, it did not have a comparative positive effect on pyrolysis gas yield, as has been widely perceived. Although certain pyrolysis gases, such as propane and hydrogen, correlated weakly positively with the lignin concentration, the total gas yielded, both condensable and noncondensable, did not correlate at the levels of the biological lignin range.[4] To further understand the results, an additional study on the response of the devolatilization rates was carried out using thermogravimetric analysis and compared to both extracted lignin and cellulose in their pure forms. The result of this basic study showed that the amount of matter devolatilized depended more upon the temperature and heat rate than the lignin concentration within the biological range. The activation energy of the reaction weakly increased with lignin content.

The alfalfa stems studied, previously described in the study by Boateng et al.,[4] were grown for fuel biomass at the Rosemount and Becker nurseries in Minnesota by the USDA–ARS Plant Science Research Unit and harvested in 2001–2003. The

set devolatilized was selected on the basis of the lignin content within a biological range spanning between 13 and 20% Klason lignin. After harvest, the alfalfa was air-dried and hand-separated to isolate the stem fractions, which were ground in a Wiley mill to an average particle size of 2 mm (passing 10 U.S. mesh). Weight loss experiments were conducted on 20 lignified alfalfa stem samples using a thermogravimetric analyzer (TGA Q series) by TA Instruments (New Castle, DE). For purposes of comparison and also to explore the full lignocellulosic range, similar experiments were conducted with pure cellulose (Aldrich) and on both alkali- and organosolv-extracted lignins. The TGA system is standard and typical, comprising a balance with a sensitivity of 0.1 μg. It employs a ceramic sample holder with a capacity of 200 mg. The platinum thermocouple was located below the sample holder and in contact with the crucible holder, while the system is purged with N_2 at flow rates in the 100–500 mL/min range. Samples of 5–10 mg of alfalfa stem fractions were loaded into the TGA furnace and pyrolyzed at three heating rates of 20, 50, and 100 °C/min and a selected final temperature of 1100 °C.

Conversion curves or extents of devolatilization, defined by $X = \lfloor m(t) - m_f \rfloor \lfloor m_o - m_f \rfloor$, where m_f is the final mass remaining and m_o is the initial mass before devolatilization, are presented in Figure 1 for the alfalfa stem samples studied, selected over the full biological range of lignin, and the control cellulose and alkali lignin samples at the three heating rates. The graphs show that rapid devolatilization of the lignified alfalfa stem biomass takes place within 250 and 400 °C and that, the greater the lignin content, the lesser the devolatilization of the biomass for all heating rates at these temperatures. At 20 °C/min heat rate, 60% volatile evolution occurred for the alfalfa stems within the 330–350 °C temperature range compared to 95% devolatilization of pure cellulose. For comparison, 60 wt % was devolatilized at rather 450 °C at this heat rate for the extracted pure alkali lignin (Figure 1a). At 50 °C/min heat rate, the majority of the volatile matter from alfalfa stems (70–80%) evolved between 340 and 370 °C depending upon the lignin content. In the comparative temperature range and heat rate, about 90% of the pure, extracted cellulose was decomposed. At this same heat rate, 70% of the pure lignin decomposed but not until 500 °C (Figure 1b). However, at a higher heat rate, i.e., 100 °C/min, the differences in the amount devolatilized became smaller (Figure 1c). The general observation is that, as the heat rate increased, the fraction volatilized from the lignified alfalfa stem samples approached that of cellulose rather than lignin. Kim

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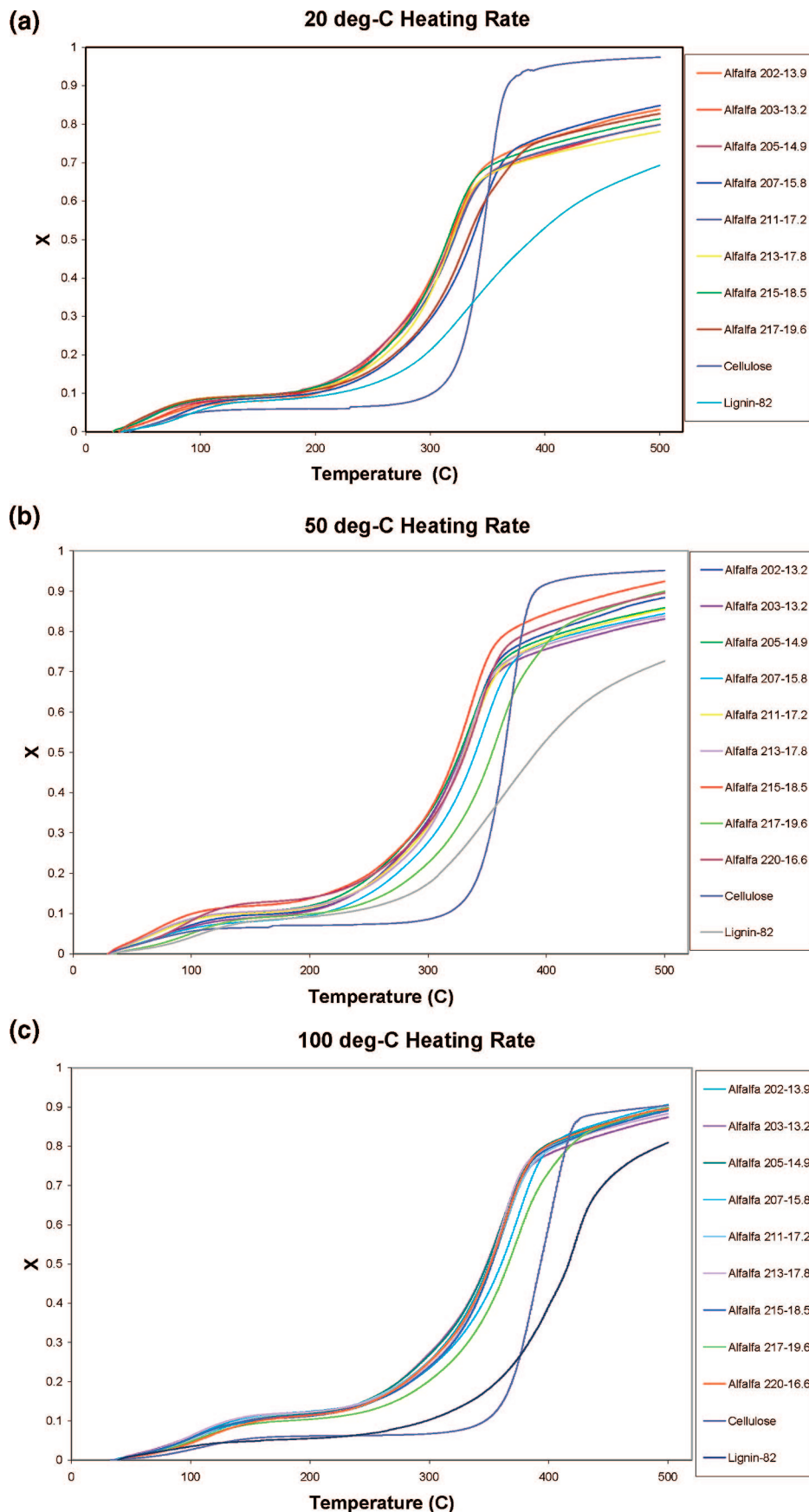
Figure 1. (a−c) Volatile evolution by thermogravimetric conversion, $X = (m - m_f)/(m_o - m_f)$ at heating rates of (a) 20 °C/min, (b) 50 °C/min, and (c) 100 °C/min. Labels indicate the sample number followed by Klason lignin content in percent.

and Agblevor[5] reported that cellulose decomposes over a 30 °C range, typically between 320 and 380 °C, which are consistent with these results. It has also been suggested that, for the devolatilization of lignocelluloses, the hemicellulose would be the first to decompose, followed by lignin and then cellulose.[6,7] When the plots presented in Figure 1 are examined on the basis of this hypothesis, it would suggest that the devolatilization of the hemicellulose and lignin fractions in the lignified alfalfa had already begun prior to 300 °C when most of the pure cellulose decomposed, i.e., when half of the potential volatile matter in the alfalfa stems evolve. However, the fraction devolatilized prior to 300 °C was considerably higher than that of the pure lignin at all heat rates. Within the rapid devolatilization temperature window, i.e., 250 and 400 °C, the amount of volatile evolved from the lignified alfalfa stems decreased with an increasing lignin content somehow, suggesting a correlation with increasing activation energy. While pure cellulose decomposed late compared to alfalfa stems, over 92% conversion was achieved by 400 °C compared to about 70−78% for the alfalfa stems and 53% or less for the extracted lignin at most of the heat rates studied. Except for the pure lignin, volatile evolution beyond 400 °C could be attributed to the devolatilization of the charcoal remaining. By 500 °C, the total amount of the alfalfa stem devolatilized approached that of the pure extracted cellulose sample.

Activation energy (E) for the devolatilization reaction was estimated from the curves presented in Figure 1 using the TA software. The results indicated that E for the devolatilization of the pure, extracted cellulose sample at 20% conversion (onset of the reaction) was about 113 kJ/mol and that for the extracted alkali lignin at the same conversion was 59 kJ/mol. For the alfalfa stem biomass, E at the onset of the devolatilization reaction ranged from a low of 91 kJ/mol to a high of 188 kJ/mol. Several values of the activation energy of biomass devolatilization have been reported in the literature.[8−10] Antal
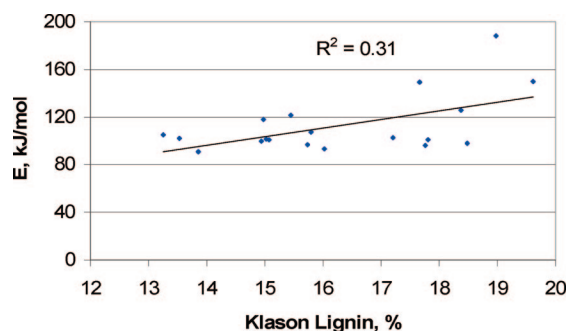
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Figure 2. Activation energy of the devolatilization reaction for lignified alfalfa stems in the biological lignin range.

et al.[9] have reported values for pure cellulose to average around 228 kJ/mol, about one-half of that estimated in this study. However, Milosavljevic and Suuberg[11] have reported low activation energies in the 140−155 kJ/mol for pure cellulose devolatilized at a high temperature, which is more consistent with this study. For lignin, Ferdous et al.[12] have reported several values of activation energy for the devolatilization of pure lignin ranging between 54 and 79 kJ/mol. There are no values reported for alfalfa stems, but data exist for lignocellulosic biomass, a majority of which is in the reported range herein. Figure 2 presents the correlation between the activation energy estimated for the devolatilization of alfalfa stems in this study and the lignin content. As is seen here, activation energy of the reaction increases only weakly linearly with an increased lignin concentration within the biological lignin range and that there appears to be no discernible correlation between the data R^2 = 0.31 for 10−20% conversion. The results suggest that, in an up-scaled thermochemical conversion process where higher heating rates of greater order and high temperatures are encountered, the biological lignin range may not be a significant factor in total gas yield, although the devolatilization pathways are inherently different.

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